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**EUROPEAN PATENT APPLICATION**

21 Application number: 81302409.8

51 Int. Cl.<sup>3</sup>: **A 61 K 6/08**  
**C 08 L 33/00**

22 Date of filing: 01.06.81

30 Priority: 29.09.80 US 191939

43 Date of publication of application:  
14.04.82 Bulletin 82/15

84 Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE

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54 **Dental restorative compositions.**

57 Two-paste dental restorative compositions cured by a free-radical-generating peroxide/amine redox combination contain either or both of ethoxylated bisphenol A dimethacrylate and propoxylated bisphenol A dimethacrylate, optionally blended with bisphenol A/glycidyl methacrylate adduct, as a monomeric matrix and one or more inorganic fillers selected from strontium aluminium borosilicate, barium aluminium silicate, barium aluminium borosilicate and mixtures thereof.

**EP 0 049 559 A2**

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1 DENTAL RESTORATIVE COMPOSITIONSDESCRIPTION

5 This invention relates to dental restorative materials. Since dentistry was first practised, dentists and patients alike have sought the ideal restorative material and the search still continues. The literature shows that many innovations have been published and patented, some of much greater significance than others.

10 However, within the past decade, composite materials based upon vitreous filled combinations of acrylic functional monomers, pioneered by R.L. Bowen and described in U.S. Patent Specification 3,006,112, have gained both professional and public acceptance and have proliferated in ever-increasing variations. Within this  
15 proliferation, certain desirable and virtually essential characteristics have become generally recognised and established, namely, (i) two-paste equi-ratio mixing, (ii) pre-shaded compositions for easy placement preparation, (iii) a sufficient radiopaque filler content to  
20 enable certain radiographic detection to be effected, (iv) adequate shelf stability, (v) physical properties approaching or even exceeding those of human tooth enamel and (vi) relative ease of finishing.

25 One characteristic of restorative compositions, which is highly desirable when used for anterior restorations and is virtually essential when used for posterior restorations, especially in occlusal load-bearing loca-

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1 tions, is sufficient abrasion-resistance to ensure  
maintenance of reasonable anatomical form for a  
duration of several years. Compared with the abrasion  
resistance of the better amalgam restorations, this  
5 characteristic has generally remained elusive during  
more than 15 years of development of dental composites.  
While masticatory forces normally serve to burnish and  
polish the occlusal surface of amalgam restorations,  
in the case of composite restorations, a two-phase  
10 erosion pattern is observable, whereby progressive  
erosion of the polymeric matrix results in eventual  
dislodgement of filler particles and this exposes new  
areas of the matrix to the erosion process.

In order to retard this erosion process  
15 significantly, changes in the characteristics of both  
the polymeric and vitreous phases appear to be necessary.  
The polymeric phase should remain relatively  
rigid, yet be less brittle and therefore tougher. This  
predicates monomer molecules of fairly rigid structure,  
20 low polymerization shrinkage and optimum crosslinking  
density. The filler particles should be of optimum  
particle size distribution for maximum volume fraction  
packing, have adequate hardness yet not be brittle and  
should closely match the refractive index of both tooth  
25 enamel and the polymeric matrix to ensure reasonable  
aesthetic appeal.

Traditionally, the vast majority of composite  
dental restoratives have embodied a monomeric matrix  
consisting of BisGMA resin, i.e. bisphenol A/glycidyl  
30 methacrylate adduct resin, diluted to a suitable  
viscosity with one or more diacrylate functional monomers.  
Most of these diluent monomers are of relatively  
low molecular weight, resulting in high polymerization  
shrinkage, high crosslinking density and brittleness  
35 due to residual matrix stress and high modulus, even-

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1 tually forming micro-cracks. Following later work,  
R.L. Bowen reported the synthesis of a liquid  
eutectic monomer blend based on isomeric phthaloyl  
dimethacrylates, but as yet this has not achieved  
5 commercial utility due to several inherent disadvantages.

There is thus a continuing need for  
improved abrasion-resistant dental composites which  
overcome the above-noted disadvantages and this  
10 invention seeks to provide such improved dental  
composites, advantageously in the form of two-paste  
systems.

The use of crystalline monomers, wholly or  
as diluents for BisGMA resin, has received little  
15 attention, particularly the use of crystalline monomers  
of closely-related structure and molecular weight.  
It has surprisingly been discovered that both ethoxylated  
and propoxylated bisphenol A dimethacrylates can  
be obtained in a very pure crystalline state, by  
20 reacting bisphenol A with either ethylene or propylene  
carbonate as appropriate, followed by esterification,  
though slight traces of impurities cause liquification  
at ambient temperature due to their low melting point.  
When optionally blended in widely variable proportions  
25 with BisGMA resin at slightly elevated temperature,  
dissolution occurs and the resulting solution remains  
stable with respect to freedom from crystal deposition,  
even after prolonged refrigeration. Furthermore,  
following easy and rapid ambient temperature copoly-  
30 merization, a tough moderately-crosslinked fracture-  
resistant polymer results, with low attendant polymerization  
shrinkage.

According to one aspect of this invention,  
therefore, a dental restorative composition is provided,  
35 which is curable by means of a free-radical-generating

1 peroxide/amine redox combination and comprising an  
acrylic functional monomer and at least one filler  
material, which is characterized in that the monomer  
comprises at least one alkoxyated bisphenol A  
5 dimethacrylate and that the filler material is selected  
from strontium aluminium borosilicate, barium aluminium  
silicate, barium aluminium borosilicate and mixtures  
thereof.

The compositions of the present invention  
10 may advantageously include either or both of ethoxy-  
lated and propoxylated bisphenol A dimethacrylates,  
alone or in combination with BisGMA resin, but they do  
not comprise BisGMA resin alone. A desired concen-  
tration of ethoxylated or propoxylated bisphenol A  
15 dimethacrylate, alone or in combination, is in the range  
from 15 to 30 weight percent. The BisGMA is preferably  
present, when used, in concentrations of up to 15 weight  
percent.

If one of the above monomers or a blend of the  
20 two monomers of suitable viscosity is then highly  
loaded with fillers of optimal particle size distri-  
bution, chosen from the aforementioned particulate  
materials of suitable modulus and refractive index,  
together with the necessary catalyst and accelerator  
25 components plus optional pigments and stabilizers, a  
two-paste system can be formulated which, when adequately  
polymerized, exhibits abrasion resistance superior to  
that of all known commercial systems presently in use.  
A suitable size distribution for the filler particles  
30 is from 0.02 to 30 microns, with approximately 50 weight  
percent of the particles preferably being in the 1.0  
to 10.0 micron size range. The filler material may  
typically be present as a single material or as a mix-  
ture of materials in a total concentration of 70 to 85  
35 weight percent. The two pastes are normally always

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- 1 spatulated together, to initiate the redox reaction,  
which results in polymerization and setting of the  
material.

- Two typical examples of such two-paste  
5 systems are as follows:

EXAMPLE 1

CATALYST PASTE

ethoxylated bisphenol A dimethacrylate monomer  
BisGMA resin

- 10 benzoyl peroxide catalyst  
UV absorber  
submicron silicon dioxide  
strontium aluminium borosilicate filler

BASE PASTE

- 15 ethoxylated bisphenol A dimethacrylate monomer  
BisGMA resin  
tertiary amine accelerator  
submicron silicon dioxide  
barium aluminium borosilicate

- 20 UV absorber  
pigments

EXAMPLE 2

CATALYST PASTE

ethoxylated bisphenol A dimethacrylate monomer

- 25 benzoyl peroxide catalyst  
UV absorber  
submicron silicon dioxide  
strontium aluminium borosilicate filler

BASE PASTE

- 30 propoxylated bisphenol A dimethacrylate monomer  
tertiary amine accelerator  
UV absorber  
pigments  
submicron silica  
35 barium aluminium silicate filler

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1           A variety of synthetic vitreous materials  
based on melts containing substantial amounts of alumina  
and silica, plus a sufficient quantity of at least one  
metallic oxide designed to impart radiopacity, are  
5 preferred. Fused alumina possesses the necessary  
abrasion resistance, but is of unsuitable refractive  
index and is essentially nonradiopaque. Many porcelain  
tooth glazes also possess the necessary abrasion resis-  
tance and refractive index, but are essentially non-  
10 radiopaque. A combination of submicron silica and  
polymeric filler yields a composite which can be  
polished almost as smooth as amalgam, but has very  
poor abrasion resistance, though it is used commercially  
in at least two anterior restorative formulations. The  
15 submicron silica may typically be present in a concen-  
tration of up to 10 weight percent. It has been  
discovered that radiopaque fillers of vitreous materials  
containing substantial amounts of barium or strontium  
oxide fused with appropriate quantities of alumina and  
20 silica to yield stable leach-resistant glasses are  
particularly suitable for use with the above-described  
monomers.

The following are further Examples of various  
compositions falling within the scope of the present  
25 invention. The percentages listed in the Examples are  
by weight:

EXAMPLE 3

A two-paste filled composite restorative material  
based on the standard peroxide/amine curing system and  
30 having the following final mix composition was prepared  
by mixing and reacting the ingredients by spatulation:



1	ethoxylated bisphenol A dimethacrylate	10.475.
	bisphenol A/glycidyl methacrylate adduct	10.475
	benzoyl peroxide	0.23
	tertiary amine	0.20
5	UV absorber	0.10
	2,6-di-tertiary-butyl-para-cresol	0.02
	strontium aluminium borosilicate	<u>78.50</u>
		100.00

An abrasion rate of 1.46 microlitres/hour was measured for this material seven days from the time of mixing.

#### EXAMPLE 4

A similar two-paste composite material utilizing a peroxide/amine curing system and having the following final mix composition was prepared in a manner similar to that set forth in Example 3.

15	bisphenol A/glycidyl methacrylate adduct	16.60
	triethylene glycol dimethacrylate (inhibited)	2.27
	butylene glycol dimethacrylate (inhibited)	2.09
20	tertiary amine	0.25
	UV absorber	0.20
	benzoyl peroxide	0.09
	strontium aluminium borosilicate	<u>78.50</u>
		100.00

This composition gave an increased abrasion rate of 1.81 microlitres/hour, measured seven days from the time of mixing, compared with the materials of Example 3.

#### EXAMPLE 5

Another peroxide/amine cured two-paste composite material was prepared, having the following final mix composition, in a manner similar to that set forth in Example 3:

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1	propoxylated bisphenol A dimethacrylate	21.50
	benzoyl peroxide	0.25
	tertiary amine	0.25
	UV absorber	0.10
		0.02
5	2,6-di-tertiary-butyl-para-cresol	0.75
	FD&C-approved pigment	1.50
	submicron silicon dioxide	75.63
	strontium aluminium borosilicate	100.00

- 10 This material gave an abrasion rate of 1.55 microlitres/hour, measured seven days from the time of mixing, which was not significantly different from the material of Example 3.

EXAMPLE 6

15	A further peroxide/amine cured two-paste composite material, having the following final mix composition, was prepared in a manner similar to that set forth in Example 3.	
	ethoxylated bisphenol A dimethacrylate	18.69
20	benzoyl peroxide	0.30
	tertiary amine	0.28
	UV absorber	0.09
	2,6-di-tertiary-butyl-para-cresol	0.02
	submicron silicon dioxide	1.39
25	barium aluminium silicate	41.10
	strontium aluminium borosilicate	38.13
		100.00

- 30 This composition gave a significantly reduced abrasion rate of 1.12 microlitres/hour, measured seven days from the time of mixing, when compared with the material of Example 3.

EXAMPLE 7

- 35 An additional peroxide/amine cured two-paste composite material, having the following final mix composition, was prepared in a manner similar to that

1 set forth in Example 3:

	ethoxylated bisphenol A dimethacrylate	21.50
	benzoyl peroxide	0.30
	tertiary amine	0.30
5	UV absorber	0.10
	2,6-di-tertiary-butyl-para-cresol	0.02
	submicron silicon dioxide	1.50
	strontium aluminium borosilicate	<u>76.28</u>
		100.00

10 This material gave an abrasion rate of 1.31 microlitres/hour, measured seven days from the time of mixing, which was not significantly different from the material of Example 3.

#### EXAMPLE 8

15 Another peroxide/amine cured two-paste composite material, having the following final mix composition, was prepared in a manner similar to that set forth in Example 3:

	ethoxylated bisphenol A dimethacrylate	25.34
20	benzoyl peroxide	0.39
	tertiary amine	0.275
	UV absorber	0.115
	2,6-di-tertiary-butyl-para-cresol	0.025
	submicron silicon dioxide	8.08
25	strontium aluminium borosilicate	31.025
	barium aluminium silicate	<u>34.75</u>
		100.00

30 An abrasion rate of 1.09 microlitres/hour was measured for this material, seven days from the time of mixing.

35 These examples show not only the scope of the present invention, compared to previously-mentioned commercially-available materials, but also the effects of compositional variations on the abrasion rate of the respective materials.

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1 Many compounds may be used as typical  
ingredients serving the functions of catalyst,  
accelerator and inhibitor and/or UV absorber com-  
ponents, such as:

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CATALYSTS

dibenzoyl peroxide

lauryl peroxide

benzoyl acetyl peroxide

10 dicyclohexyl peroxide

ACCELERATORS

dimethyl-para-toluidine

diethyl-para-toluidine

dihydroxyethyl-para-toluidine

15 N,N-dimethyl-3,5-xylidine

para-(dimethylamino)-phenylacetic acid

INHIBITORS

hydroquinone monomethyl ether

2,6-di-tertiary-butyl-para-cresol

20 2-tertiary-butyl-4-methoxyphenol

3-tertiary-butyl-4-methoxyphenol

The catalysts, accelerators and inhibitors  
may typically be present in concentrations of up to  
1.0 weight percent. Other additives, such as UV  
25 absorbers, are typically present in concentrations of  
up to 0.5 weight percent.

Very many different polymeric matrix and  
filler combinations have been investigated with respect  
to abrasion resistance, using a "protomatic" toothbrush  
30 abrasion machine, fitted with Colgate-Palmolive "medium"  
toothbrush heads, running in a simulated toothpaste  
slurry at 140 strokes per minute, with a fixed load of  
220 grams and a stroke of 5.7 cm (2.25 inches) for a  
total of 67,200 strokes per specimen, over a swept area  
35 of 9.7 cm (1.5 square inches). The results obtained

- 1 for six commercial composite restoratives and the best  
 six materials (Examples 3 - 8) of the present inven-  
 tion were as follows:

TABLE

5		Microlitres/ hour Abrasion Rate**
	"Silar" * (Microfilled) 3M Company	19.80
	"Vytal" * L.D.Caulk Co.	3.33
	"Profile" * S.S.White	2.34
10	"Simulate" * Sybron/Kerr	2.17
	"Concise" * 3M Company	2.15
	"Adaptic" * (Radiopaque) J & J	1.95
	Strontium glass/BISGMA/TEGDMA/BGMA	1.81
	Strontium glass/FBPADMA	1.55
15	Strontium glass/EBPADMA/BISGMA	1.46
	Strontium glass/EBPADMA	1.31
	Strontium glass/barium aluminosilicate/EBPADMA	1.12
	Strontium glass/barium aluminosilicate/FBPADMA	1.09

\* Trademark of respective company listed in Table

20 \*\* Measured seven days from time of mixing

It is readily seen that the abrasion  
 resistance of commercial composites varies considerably  
 and even the worst have been claimed to be satisfactory  
 in clinical studies using anterior teeth and selected  
 25 classes of cavity. Among the materials of the present  
 invention, namely the last six materials listed in the  
 Table, it can be seen that for a given filler system the  
 abrasion resistance is always greater for the polymeric  
 matrixes of this invention and that the commercially  
 30 available radiopaque vitreous fillers utilized indicate  
 that strontium-containing fillers generally exhibit  
 superior abrasion resistance.

1 CLAIMS:

1. A dental restorative composition curable  
by means of a free-radical-generating peroxide/amine  
redox combination and comprising an acrylic functional  
5 monomer and at least one filler material,  
characterised in  
that the monomer comprises at least one alkoxyated  
bisphenol A dimethacrylate and that the filler material  
is selected from strontium aluminium borosilicate,  
10 barium aluminium silicate, barium aluminium borosilicate  
and mixtures thereof.
2. A dental restorative composition according  
to claim 1, wherein the monomer comprises ethoxylated  
bisphenol A dimethacrylate.
- 15 3. A dental restorative composition according  
to claim 1 or 2, wherein the monomer comprises propoxy-  
lated bisphenol A dimethacrylate.
4. A dental restorative composition according  
to claim 1, 2 or 3, wherein the monomer is either or both  
20 of ethoxylated bisphenol A dimethacrylate and propoxy-  
lated bisphenol A dimethacrylate blended with bis-  
phenol A/glycidyl methacrylate adduct.
5. A dental restorative composition according  
to any preceding claim, which comprises 15-30 weight  
25 percent of ethoxylated bisphenol A dimethacrylate and/or  
prepoxyated bisphenol A dimethacrylate blended with  
bisphenol A/glycidyl methacrylate adduct and 70-85 weight  
percent of the filler material.
6. A cured composite dental restoration  
30 composition comprising an acrylic functional monomer  
and at least one filler material,  
characterised in  
that the cured composition consists essentially of:  
(a) 15-30 weight percent of at least one  
35 material selected from ethoxylated bisphenol A dimeth-

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- 1 acrylate and propoxylated bisphenol A dimethacrylate;  
     (b) up to 15 weight percent of bisphenol  
 A/glycidyl methacrylate adduct;  
     (c) an activator;  
 5      (d) a catalyst;  
     (e) 70-85 weight percent of filler material  
 selected from strontium aluminium borosilicate, barium  
 aluminium silicate, barium aluminium borosilicate and  
 mixtures thereof.
- 10           7. A cured two-paste filled composite  
 restorative material based on the standard peroxide/  
 amine curing system and having the following final  
 mix composition by weight:
- |   |   |                |
|---|---|----------------|
| ethoxylated bisphenol A dimethacrylate      | ) |                |
| 15 bisphenol A/glycidyl methacrylate adduct | ) | 15-30 combined |
| benzoyl peroxide                            |   | 0.1-1.0        |
| tertiary amine                              |   | 0.1-1.0        |
| UV absorber                                 |   | 0.05-0.50      |
| 2,6-di-tertiary-butyl-para-cresol           |   | 0.01-0.10      |
| 20 strontium aluminium borosilicate         | ) |                |
| barium aluminium borosilicate               | ) | 70-85 combined |
| TOTAL                                       |   | 100.00         |

8. A cured two-paste composite material  
 having the following final mix composition by weight:
- |  |           |
|--|-----------|
| 25 propoxylated bisphenol A dimethacrylate | 15-30     |
| benzoyl peroxide                           | 0.1-1.0   |
| UV absorber                                | 0.05-0.50 |
| 2,6-di-tertiary-butyl-para-cresol          | 0.01-0.10 |
| submicron silicon dioxide                  | 1.0-10.0  |
| 30 barium aluminium silicate               | 70-85     |
| TOTAL                                      |           |
| 100.00                                     |           |

9. A peroxide/amine cured two-paste  
 composite material having the following final mix  
 composition by weight:
- 35

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1	ethoxylated bisphenol A dimethacrylate	15-30
	benzoyl peroxide	0.1-1.0
	tertiary amine	0.1-1.0
	UV absorber	0.05-0.50
5	2,6-di-tertiary-butyl-para-cresol	0.01-0.10
	submicron silicon dioxide	1.0-10.0
	barium aluminium silicate )	70-85 combin-
	strontium aluminium borosilicate)	ed
	TOTAL	100.00

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